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(54) A METHOD OF PRODUCING ARYLENEPHENOL-FORMALDEHYDE RESINS AND MOULDING MATERIAL ON THE BASIS THEREOF

(71) We, NAUCHNO-ISSLEDOVATELSKY INSTITUT PLASTICHESKIKH MASS, a State Enterprise, organised and existing under the Laws of the Union of Soviet Socialist Republics, of E-112, Moscow, Union of Soviet Socialist Republics, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to methods of producing arylene phenol - formaldehyde resins (phenoformolites) containing aromatic hydrocarbons. Phenoformolites belong to the class of thermosetting resins and can harden, passing into three-dimensional infusible insoluble structures.

It is also an object of the invention to employ the obtained phenoformolites in the production of a moulding material.

Known in the art are a number of two-stage methods of producing phenoformolites, comprising synthesizing formolites by condensation of aromatic hydrocarbons with formaldehyde in strongly acidic media (25—45% H_2SO_4), and subsequently synthesising of the phenoformolites by condensing the washed neutralized formolites with phenol and an additional amount of formaldehyde.

Also known is a method of producing phenoformolites by the cocondensation of reactive aromatic hydrocarbons with phenol and formaldehyde. The process is carried out in the presence of sulphuric and hydrochloric acid, the concentration of which at the end of the reaction should be not less than 15—20%.

The disadvantages inherent in the known methods are as follows.

The necessity to dispose of tremendous amounts of spent sulphuric acid, as well as to wash and neutralize formolites; the necessity of employing special acid-resistant equipment and communications, both for the two-stage and single-stage methods; the impossibility of using polycyclic hydrocarbons which feature a high melting point, *per se*, such hydrocarbons being usually used in the form of solutions in liquid aromatic hydrocarbons.

The object of the present invention is to obviate or mitigate the above disadvantages.

According to the invention there is provided a method of producing an arylene phenol-formaldehyde resin, comprising condensing a eutectic or natural polyeutectic mixture of aromatic hydrocarbons with phenol and formaldehyde in the presence of an acid catalyst.

The reactivity of said mixtures is close to that of phenol, as has been shown by the investigation of the initial rates with which these mixtures react with formaldehyde. The close reaction rates of eutectic and natural polyeutectic mixtures of hydrocarbons and phenol with formaldehyde make it possible to effect the process in one stage, obviating the need to separate the formolite.

Moreover, the method of the present invention makes it possible to considerably reduce the consumption of the acid catalyst and to

[*Price 25p*]

use high-melting aromatic hydrocarbons and technical mixtures of aromatic hydrocarbons (natural polyeutectic mixtures) which have not been employed heretofore.

Since the melting point of eutectic mixtures is considerably lower than the melting point of individual hydrocarbons, the method of producing phenoformolites proposed herein enables the use of practically any hydrocarbon of the aromatic series.

As eutectic mixtures use may be made, for example, of mixtures of pyrene and fluoroanthene, pyrene and naphthalene, pyrene and coronene, naphthalene and phenanthrene. In addition to artificial mixtures it is also possible to employ technical mixtures which are complex polyeutectic systems, such as crude anthracene.

The ratio between the eutectic or polyeutectic mixture, phenol and formaldehyde may be varied within a wide range. Most expedient in this respect prove to be weight ratios equal to 1:1—2:0.287—0.575, (from 1:1:0.287 to 1:2.0.575).

An acid catalyst is recommended to be taken in the process in an amount equal to 0.1—2% of the total weight of the reagents.

If eutectic or polyeutectic mixtures whose melting point is below 100°C are used, it is advisable to use formaldehyde in the form of a 35—38% aqueous solution thereof.

If the eutectic mixtures used have a melting point above 100°C, it is recommended that formaldehyde oligomers should be employed as the source of formaldehyde.

Phenoformolites produced by the present method may be successfully used as a binder in the production of both general-purpose moulding material which require organic fillers, such as wood flour, and special-purpose moulding material containing mineral fillers. The composition of the moulding material is made in accordance with conventionally adopted formulations, and the ratio between the ingredients in this composition (a binder, organic or mineral fillers and hardeners) is within the generally known adopted ranges. The moulding material based on phenoformolites may be formed into articles by press moulding or injection moulding. The presence in phenoformolites of aromatic hydrocarbons with condensed nuclei makes it possible to produce articles featuring high dielectric and thermophysical characteristics.

The method proposed herein may be carried out without any additional capital investiments, on existing equipment employed in plants producing plastics, and in accordance with the flow sheets now in use. The employment of small amounts of catalysts makes it unnecessary to utilize special acid-resisting equipment.

For a better understanding of the present invention, given hereinbelow are examples illustrating the producing of arylenephenolformaldehyde resins and their application.

EXAMPLE 1

A vacuum cooker is charged with 19.6 parts by weight of fluoranthene, 8.4 parts by weight of pyrene, 42 parts by weight of phenol, 9.6 parts by weight of α-polyoxymethylene and 0.5 part by weight of $ZnCl_2$. The condensation is carried out at 95—100°C with constant stirring for 5 hours. The resin obtained is vacuum-dried and drained.

EXAMPLE 2

A three-necked flask equipped with a reflux condenser, a thermometer and a stirrer is charged with 22.4 parts by weight of coronene, 5.6 parts by weight of pyrene, 56 parts by weight of phenol, 15 parts by weight of α-polyoxymethylene and 1 part by weight of $ZnCl_2$. The polycondensation is carried out at a temperature of 105—110°C with constant stirring for 5 hours. The resin obtained is discharged into an evaporating dish and dried.

EXAMPLE 3

A vacuum cooker is charged with 20 parts by weight of crude anthracene, 40 parts by weight of phenol, 35 parts by weight of formalin (36.7%) and 1 part by weight of hydrochloric acid (sp. gr. 1.19). The reaction mass is heated up to the boiling point with constant stirring and kept at a temperature of 95—100°C for 2 hours, whereupon the resin is dehydrated under a vacuum and drained.

The properties of the phenoformolites obtained in the above Examples are listed in Table 1.

TABLE 1

Characteristics	Phenoformolite based on crude anthracene	Phenoformolite based on eutectic mixture of fluoranthene and pyrene	Phenoformolite based on eutectic mixture of coronene and pyrene
Rate of gelation on plate at 160°C with 10% of urotropin, sec.	60—80	80—90	60—70
Amount of extracted substances in alcohol-benzene mixture, 1:1, per cent	2—3	2—3	2—3
Coking index, per cent	60—63	65—67	70—72
Ubbelohde drop point, °C	110—120	104—106	110—115
Losses in weight when testing on derivatograph: 100°C	0	0	0
200°C	0	0	0
300°C	1.9	1.7	1.1
400°C	5.5	5.3	4.2
500°C	23.7	23.2	20.8

EXAMPLE 4

On the basis of the phenoformolites produced as described in Examples 1—3 compositions are prepared, comprising (in per cent by weight): phenoformolite (resin) — 42.8, urotropin — 6.5, kaolin — 1.5, — nigrosine — 1.5, lime — 0.9, stearine — 0.7, wood flour — 43.2. The compositions are rolled on continuous-action rolls with the gap therebetween equal to 1—2 mm. The resulting sheets of the rolled material are comminuted and used for press moulding.

The properties of the moulding materials produced as described in Example 4 are presented in Table 2.

TABLE 2

Characteristics	Moulding material based on resin made from crude anthracene	Moulding Material based on resin made from fluoranthene and pyrene	Moulding Material based on resin made from coronene and pyrene
Specific impact strength, kg.cm/cm^2	6.5	5.5	5.9
Static bending strength, kg/cm^2	749	758	773
Brinell hardness, kg/mm^2	65	66	71
Martens thermostability, °C	187	186	189
Water absorption, per cent	0.018	0.013	0.009
Surface resistance, ohm	2.9×10^{15}	2.8×10^{15}	3.8×10^{15}
Volume resistance, ohm.cm	3.7×10^{11}	3.7×10^{11}	4.5×10^{11}
Dielectric constant	4.5	4.5	4.9
Dielectric power factor	0.025	0.022	0.017
Average breakdown voltage, kV/mm	14.8	15.3	15.9

WHAT WE CLAIM IS:—

1. A method of producing an arylene phenol-formaldehyde resin, comprising condensing a eutectic or natural polyeutectic mixture of aromatic hydrocarbons with phenol and formaldehyde in the presence of an acid catalyst.

2. A method as claimed in claim 1, wherein the condensation is carried out with the weight ratios between the eutectic or natural polyeutectic mixture of aromatic hydrocarbons, phenol and formaldehyde being equal to 1:1—2:0.287—0.575 (1:1:0.287 to 1:2:0.575).

3. A method as claimed in claims 1 and 2, wherein the amount of acid catalyst used is from 0.1 to 2% of the total weight of the reagents.

4. A method as claimed in claims 1, 2 or 3 using a eutectic or natural polyeutectic mixture with a melting point below 100°C, wherein formaldehyde is employed in the form of a 35—38% by weight aqueous solution thereof.

5. A method as claimed in claim 1, 2 or 3, using a eutectic mixture with a melting point above 100 C, wherein formaldehyde oligomers are used as the source of formaldehyde.

6. A method of producing an arylene phenol-formaldehyde resin according to any one of the Examples.

7. Arylene phenol-formaldehyde resins whenever produced by the method claimed in any one of claims 1 to 6.

8. A moulding material including as a binder, an arylene phenol-formaldehyde resin as claimed in claim 7.

9. A moulding material according to claim 8 including also an organic or mineral filler and a hardener to produce a material suitable for injection or press moulding.

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